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THE FIRST NATURALLY OCCURRING PHYTYL ESTERS AND HEXANE SOLUBLE NON-VOLATILES FROM LEAVES OF *FATSIA JAPONICA*

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Key Word Index—*Fatsia japonica*, Araliaceae, phytyl palmitate, phytyl linoleate; phytol, stigmasterol; fatty acids, alkanes

Plant. Fatsia japonica Decne. et Planch. (Araliaceae) (Japanese name, yatsude). *Source.* Hiroshima Prefecture, Japan. *Uses.* Folk remedies.[1] *Previous work.* On saponins from the leaves[1–3] and the roots[3] and on steam-distillates from the leaves.[4]

Present work. The *n*-hexane soluble non-volatile fraction of the acetone extract from the leaves of *F. japonica* was found to be composed of phytyl palmitate, phytyl linoleate, phytol, stigmasterol, fatty acids ($C_{16}H_{32}O_2$, $C_{18}H_{36}O_2$, $C_{18}H_{32}O_2$ and $C_{18}H_{30}O_2$) and *n*-alkanes ($C_{16} \sim C_{31}$). The two esters are the first reported naturally occurring esters of phytol. These phytyl esters were characterized on the basis of an appearance of characteristic ester bands in their IR spectra and an occurrence of phytol and the fatty acids on saponification.

EXPERIMENTAL

IR spectra were taken in KBr pellets or as liquid films NMR spectra were run on a Hitachi–Perkin–Elmer model R-20 spectrometer at 60 MHz in a $CDCl_3$ soln using TMS as internal standard The GLC of the fatty acid methyl esters was carried out on a Hitachi model F-6D chromatograph using standard conditions MS were obtained on a Hitachi RMS-4 mass spectrometer at 80 eV

Extraction and isolation The leaves of *F japonica* (14 kg) were collected in March and dipped in acetone at room temp for 3 months to extract their constituents. The acetone extract was concentrated to dryness to give a viscous oily substance, which was then extracted with *n*-hexane The *n*-hexane soluble fraction was treated with 5% $NaHCO_3$ to give neutral (6 g) and acidic fractions (0 28 g) The neutral fraction was chromatographed on a silica gel column with *n*-hexane–EtOAc as eluent with increasing EtOAc concn, giving in order normal alkanes (10 mg), a mixture of phytyl esters (710 mg), phytol (950 mg) and stigmasterol (169 mg). The mixture of the esters was further chromatographed on an $AgNO_3$-impregnated silica gel column to give in order phytyl palmitate (180 mg) and phytyl linoleate (444 mg)

Identification of the compounds Phtyl palmitate $C_{36}H_{70}O_2$; n_D^{25} 1·4540; $[\alpha]_D^{25}$ +9 7° (*c* 0·513, $CHCl_3$); ν_{max} (liquid) 1740, 1170 cm^{-1} (ester –CO–O–), δ_{ppm} 1 67 (*s*, 3H, >C=CC<u>H</u>$_3$–), 2·37 (*t*, *J* 6Hz, 2H, –CO–C<u>H</u>$_2$–CH$_2$–), 4 58 (*d*, *J* 7Hz, 2H, >C=CH–C<u>H</u>$_2$–O–), 5 27 (broad *s*, 1H, >C=C<u>H</u>–) Saponification of this ester with 5% KOH–MeOH for 1 5 hr gave phytol (characterized by co-TLC, IR and NMR) and palmitic acid (identified by direct comparison of the methylated acid with an authentic sample by co-TLC and co-GLC) *Phytyl linoleate.* $C_{38}H_{70}O_2$, n_D^{25} 1 4913; $[\alpha]_D^{25}$ +21 3° (*c* 0·470, $CHCl_3$); ν_{max}(liquid) 1738, 1170 cm^{-1} (ester –CO–O–); δ_{ppm} 1·68 (*s*, 3H, >C=CC<u>H</u>$_3$–), 2·37 (*t*, *J* 6Hz, 2H, –CO–C<u>H</u>$_2$–CH$_2$–), 2 75 (*m*, 2H, =CH–C<u>H</u>$_2$–CH=), 4·59 (*d*, *J* 7Hz, 2H, >C=CH–C<u>H</u>$_2$–O–), 5 34 (*m*, 5H). Saponification of this ester under the same conditions as above furnished phytol

[1] OHTA, K (1924) *Keiō Igaku* **4**, 157

[2] OHTA, K. (1924) *ibid* **3**, 1111

[3] KOTAKE, M, TAGUCHI, K. and OKAMOTO, T (1933) *Rikagaku Kenkyusho Hōkoku* **12**, 590

[4] FUJITA, Y., FUJITA, S, KASHIMOTO, Y. and HAYASHI, R (1973) The Pre-abstract of the 17th Symposium on the Chemistry of Terpenes, Essential Oils and Aromatics of the Chemical Society of Japan, Okayama, October, p 24.

and linoleic acid These were characterized in the same manner as described above n-*Alkanes* GLC indicated the alkanes to be composed of almost equal amounts of n-$C_{16}H_{34}$ to n-$C_{31}H_{64}$ *Phytol* $C_{20}H_{40}O$, n_D^{25} 1 4637, $[\alpha]_D^{25}$ +0 98° (*c* 1 708, $CHCl_3$), *m/e* 296 (M^+), 71 (base), ν_{max}(liquid) 3300 (O–H), 1670 (C=C) 790 cm^{-1} (>C=CH–), δ_{ppm} 1 65 (s, 3H, >C=CC$\underline{H}_3$–), 4 12 (*d*, *J* 7Hz, 2H, =CH–C$\underline{H}_2$–O–), 5 38 (*t*, *J* 7Hz, 1H –C$\underline{H}$–CH_2–O–) direct comparison (co-TLC, IR, NMR and MS) with a known sample *Stigmasterol* $C_{29}H_{48}O$, mp 168 8 170°, $[\alpha]_D^{25}$ −52 9° (*c* 0 846, $CHCl_3$), *m/e* 412 (M^+), 55 (base), ν_{max} (KBr) 3350 (O–H), 1640 (C=C), 970 (trans –CH=CH–), 840 cm^{-1} (>C=C$\underline{H}$–), δ_{ppm} 5 09 (*t*, *J* 3Hz, 2H), 5 37 (broad s, 1H), direct comparison (m.m.p., co-TLC, IR, NMR and MS) *Fatty acids* The acidic fraction (0 28 g) was methylated with CH_2N_2 The methylated acids were then subjected to co-GLC with authentic samples The acidic fraction was thus found to be composed of palmitic acid (33 2%), stearic acid (18 6%), linoleic acid (15 6%), linolenic acid (20 4%) and other acids (14 2%)

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TWO PENTAMETHOXYLATED FLAVONOIDS FROM *GYMNOSPERMA GLUTINOSUM*

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Key Word Index—*Gymnosperma glutinosum*, Compositae, essential oil, phellandrene, camphene, α-pinene, 5,7-dihydroxy-6,8,3′,4′,5′-pentamethoxyflavone (luiselizondin), 5-hydroxy-3,6,7,8,3′-pentamethoxyflavone, emmaosunin

Plant Gymnosperma glutinosum (Spreng) (Syn. *Selloa glutinosum*, (Spreng)) Tatalencho, xonoquilitl (Voucher specimen No. 7268). Collected in San Luis Potosi in February 1972. Is a monotypic genus. *Uses* The flower heads as a cure of rheumatic illness.[1]

Previous work. None.

Steam distillation The semidried aerial part was steam distilled, a colorless, odiferous oil was obtained (yield 0 7%), sp. gr. 0 92, $\eta_D^{22°}$ 1 4725, $[\alpha]_D^{22°}$ +17°. IR and NMR did not show aromatic or carbonyl compounds. TLC and VPC showed phellandrene, camphene and α-pinene as main components.

Extraction. The pulverized dried aerial part was extracted with EtOH, the extract was evaporated and the residue was taken in $CHCl_3$. This solution was chromatographed on silica gel. On elution with $CHCl_3$–MeOH, two new flavonoids were successively percolated. *Luiselizondin*, as yellow crystals, m.p. 178–179°, $C_{20}H_{20}O_9$. Zeisel number gave $5CH_3O$. IR, 1650, 1620, 1585 and 1518 cm^{-1}. NMR: singlet at 7·4δ (2H), another at 6 2 (s, 1H), four singlets at 4 12 (3H), 4·08 (3H), 4 0 (6H) and 3·9 (3H), corresponding at five CH_3O groups, at down field 400 Hz there was a signal (1H). The UV in MeOH gave a spectrum typical of a flavone.[2] The addition of $AlCl_3$, $AlCl_3$–HCl and NaOAc·H_3BO_3 gave the expected displacements for a 5-hydroxyflavone. The MS gave a molecular ion at *m/e* 404 ($C_{20}H_{20}O_9$). The fragmentation pattern was as expected for a 5,7-dihydroxy-6,8,3′,4′,5′-pentamethoxyflavone,[3] a microfusion with KOH gave the expected 3,4,5-trimethoxyben-

[1] MARTÍNEZ, M. (1959) *Las Plantas Medicinales de Mexico* 4a. Ed. Botas, México, p. 299.

[2] MABRY, T. J., MARKHAM, K. R. and THOMAS, M. B. (1970) *The Systematic Identification of Flavonoids*, Springer, New York.

[3] ALDER, H. (1966) *Bull. Soc. Chim. Fr.* 2893.